Re-evaluation of HO_3 Structure Using Millimeter-Submillimeter Spectroscopy

Luyao Zou, Brian Hays,
Susanna L. Widicus Weaver
Emory University, Atlanta GA

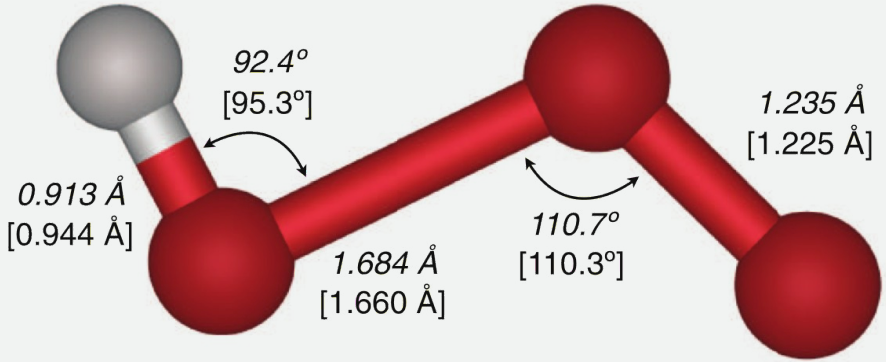
HO_3 – A Weakly Bound Radical

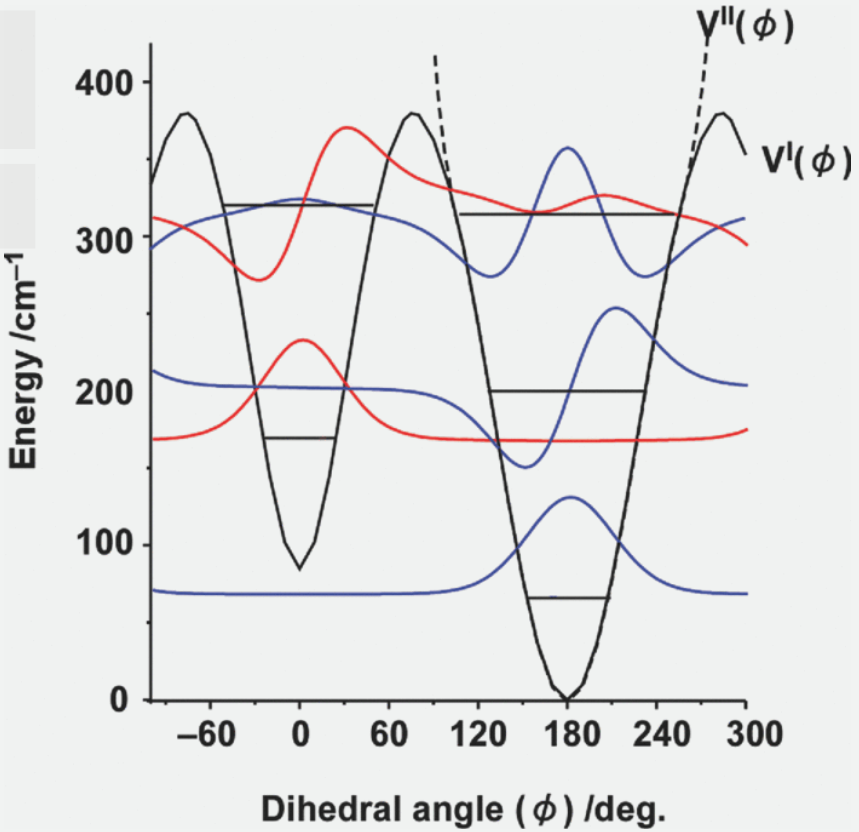
Atmospheric, Biochemical and Astrochemical Interest

Isomerization & Dissociation

Peculiar Geometry

Large Amplitude Motions



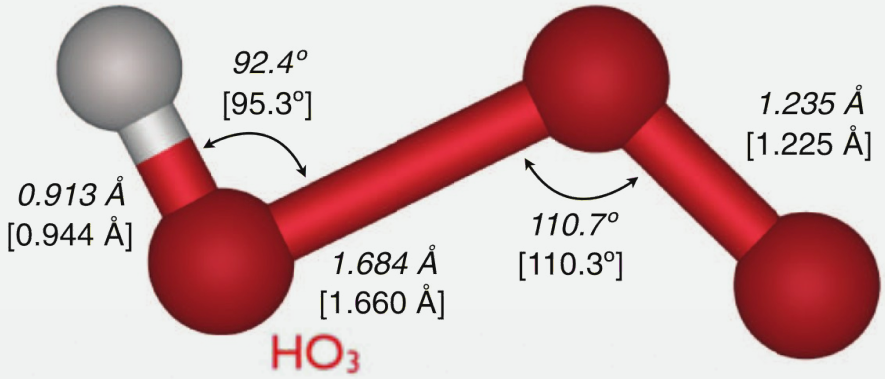


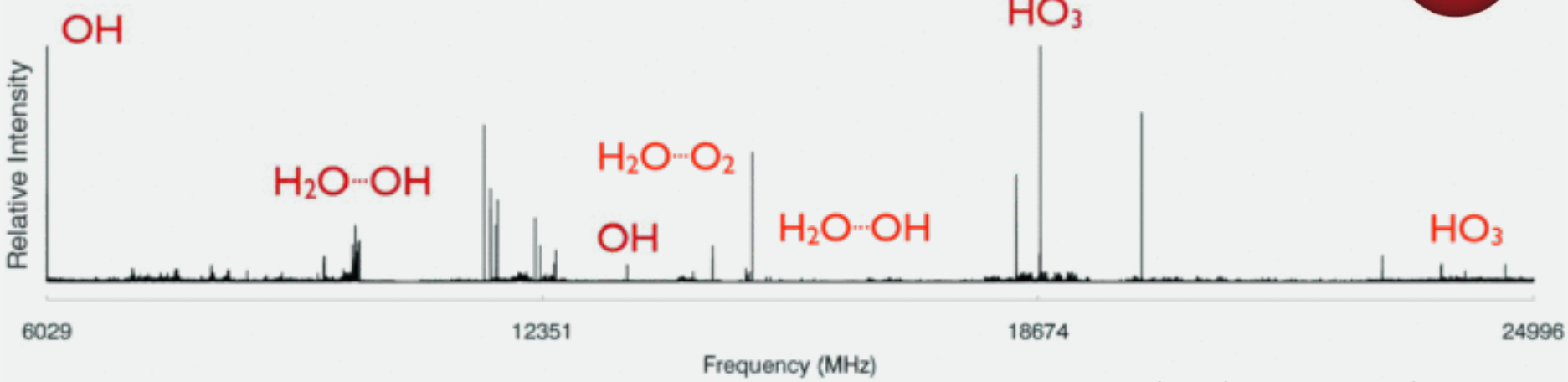
McCarthy et al., *J. Chem. Phys.*, **2012**, 136, 034303
Suma, Sumiyoshi & Endo, *J. Chem. Phys.*, **2013**, 139, 094301

HO_3 – Experimental Spectroscopic Studies

FTMW & Isotope Substitution
FTMW-mm Double Resonance

Suma et al., (2005)
McCarthy et al., (2012)





Suma, Sumiyoshi & Endo, *Science*, **2005**, 308, 1885
McCarthy et al., *J. Chem. Phys.*, **2012**, 136, 034303

Advantage of mm-submm Spectroscopy

Wider Frequency Coverage

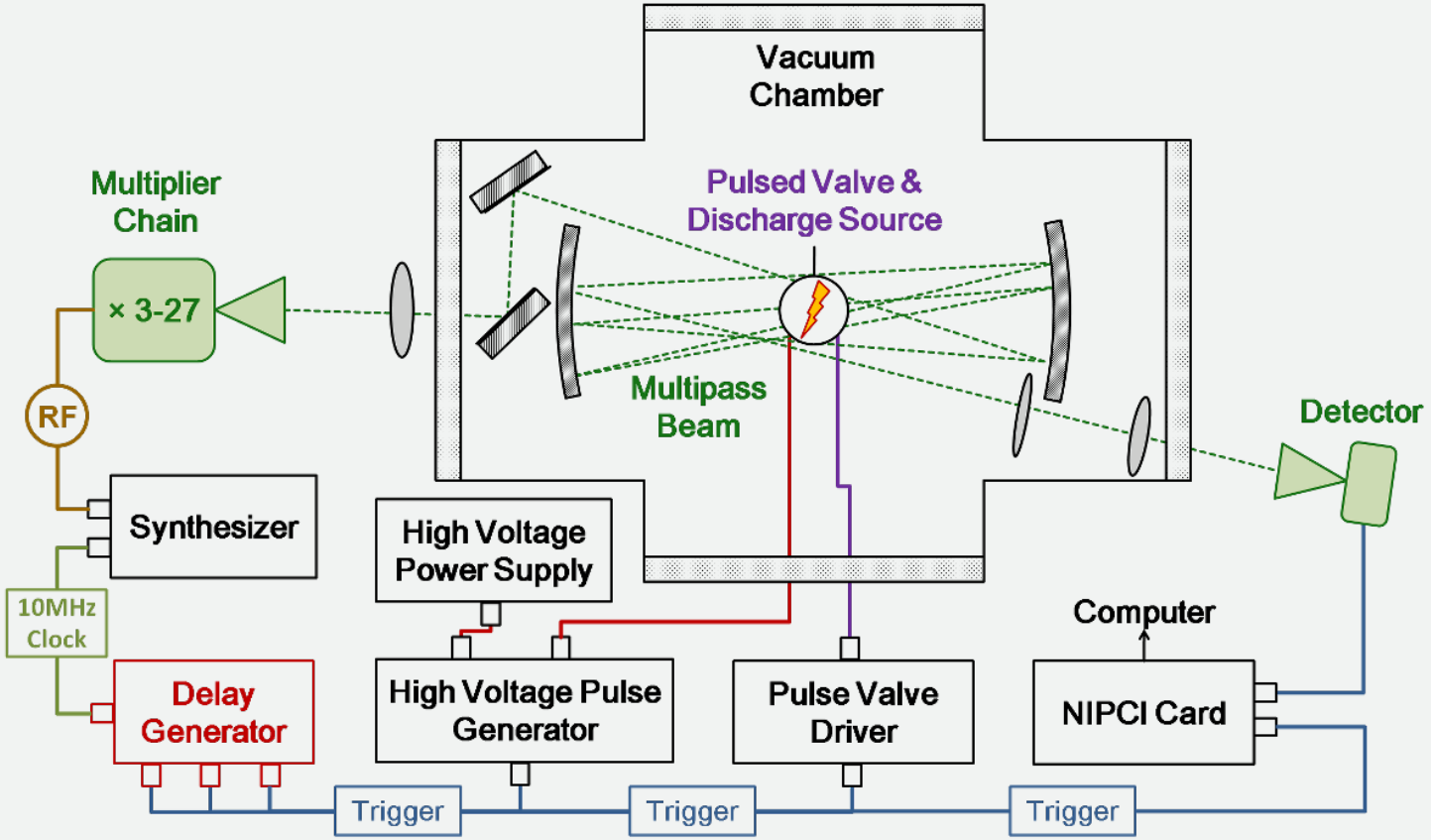
More Energy Level Access (higher K_a)

High Frequency Resolution (sub-MHz level)

Directly Comparable to
mm-submm Astronomy

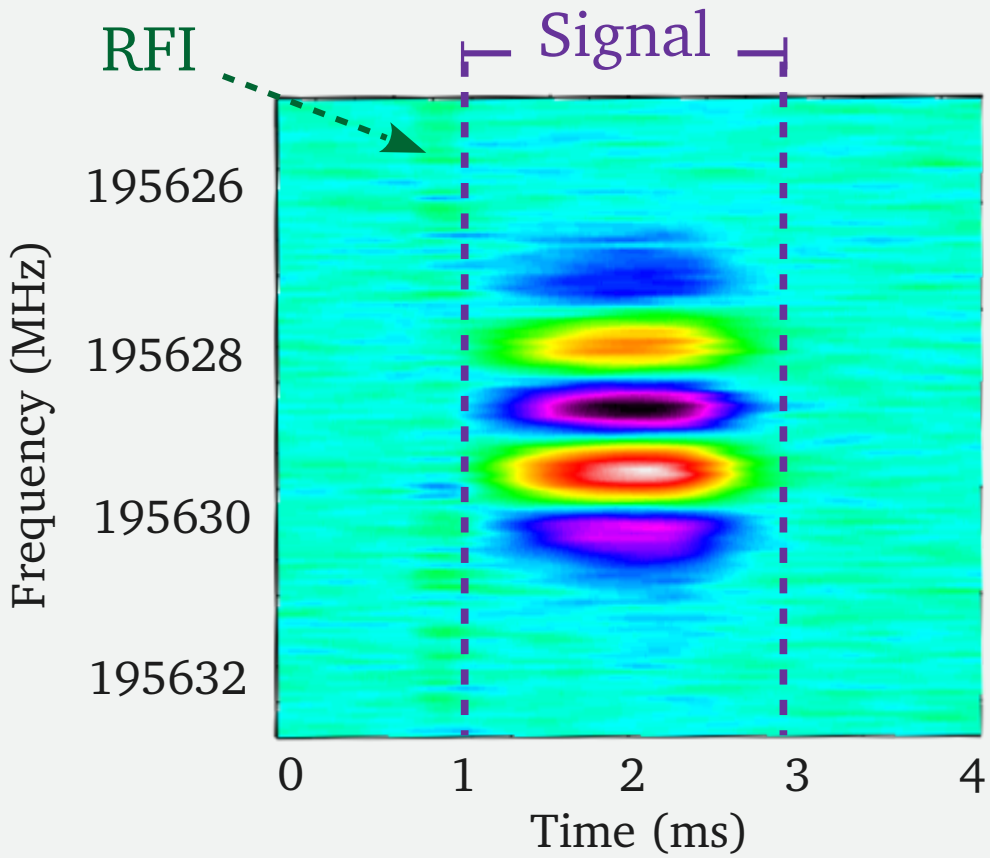
The HO_3 Experimental Setup

- Jet-cooled Expansion
- Pulsed Discharge
- 7-pass (sub)mm Beam
- 10 MHz Rb Clock
- Lock-in/Fast Sweep
- Detected Discharge Products: *trans*-HO_3, HO_2, H_2O, H_2O_2, O_3, $O_2(^1\Delta)$

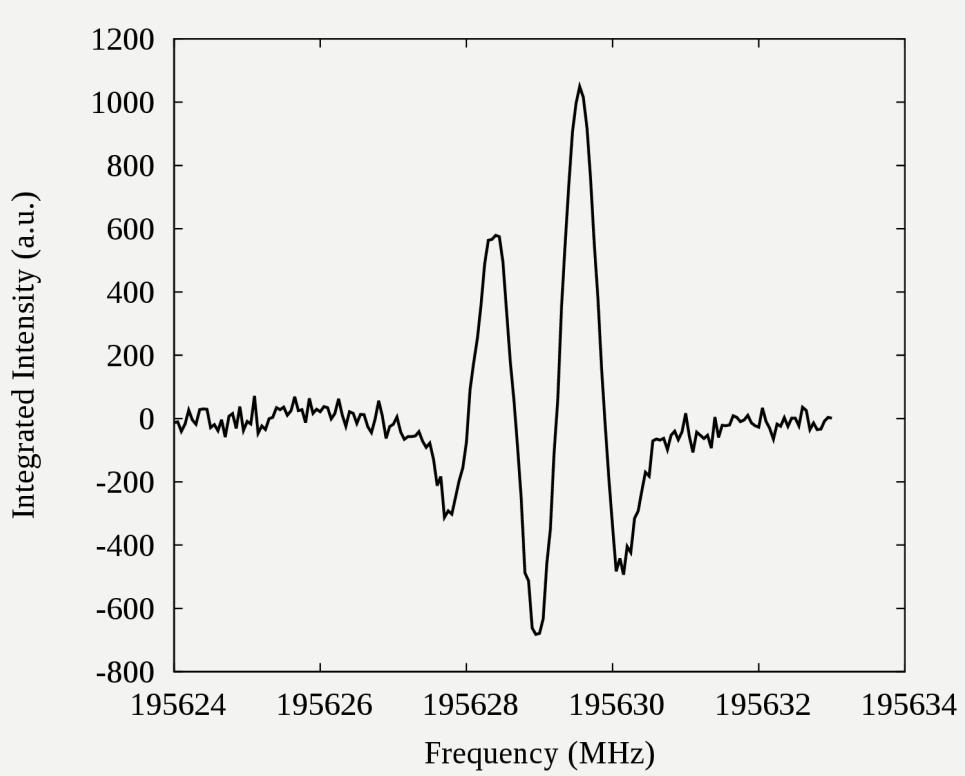


McCarthy et al., *Astrophys. J. S.*, **2000**, 129, 611
Perry et al., *Appl. Opt.*, **1990**, 29, 119; Laas et al., *J. Phys. Chem. A*, **2013**, 117, 9548

Lock-in Data Acquisition



Lock-in Data Acquisition



Advantage

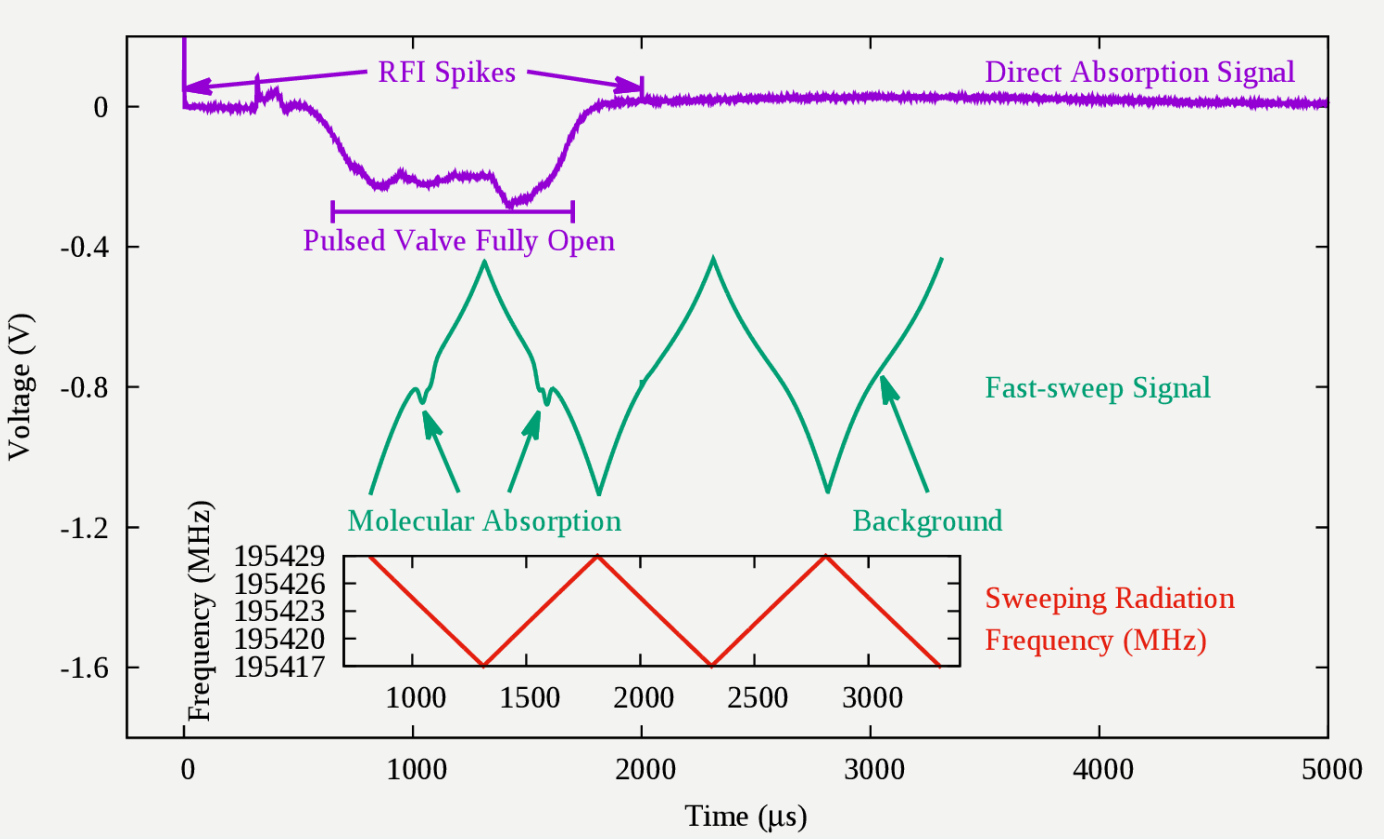
High Sensitivity: Able to detect weak transitions within a reasonable number of averages

Disadvantage

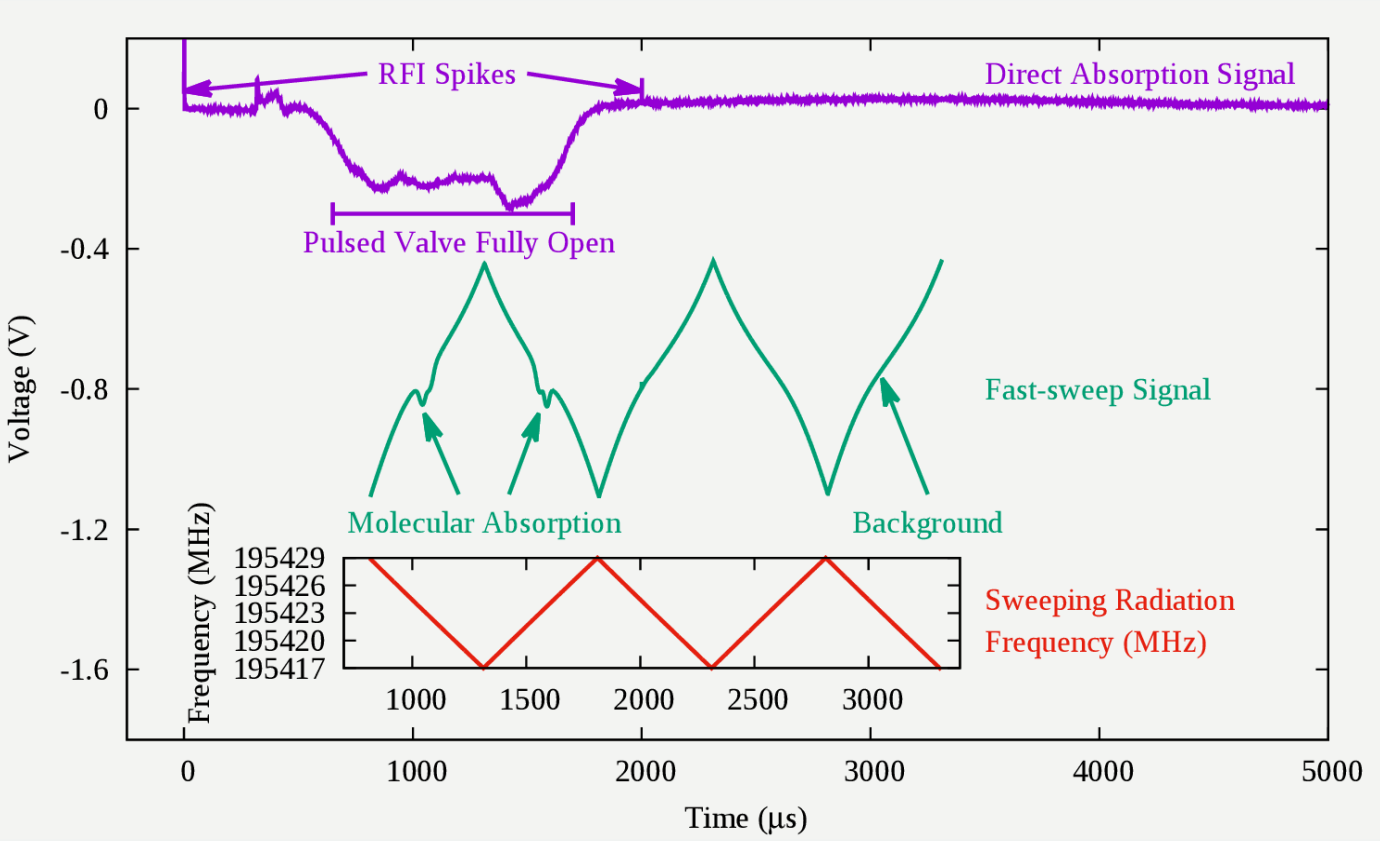
Speed: Slow

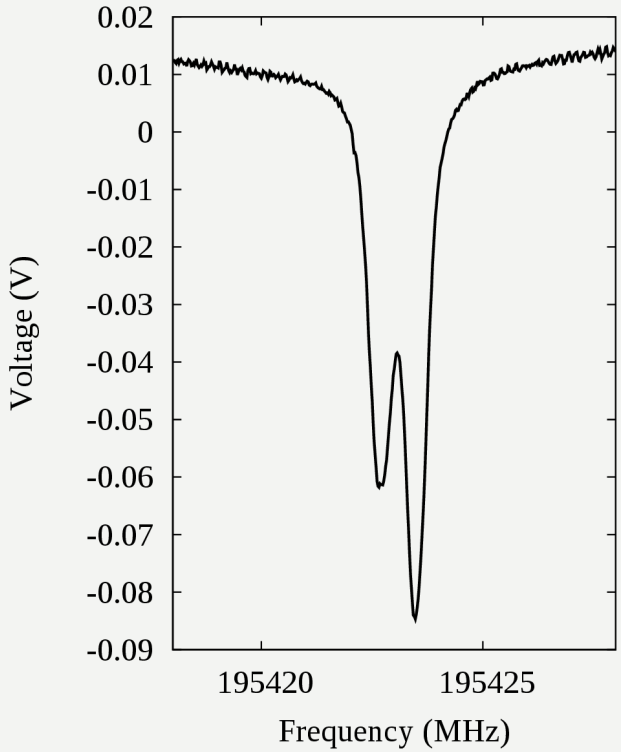
Ideal for line confirmation

Fast Sweep Data Acquisition

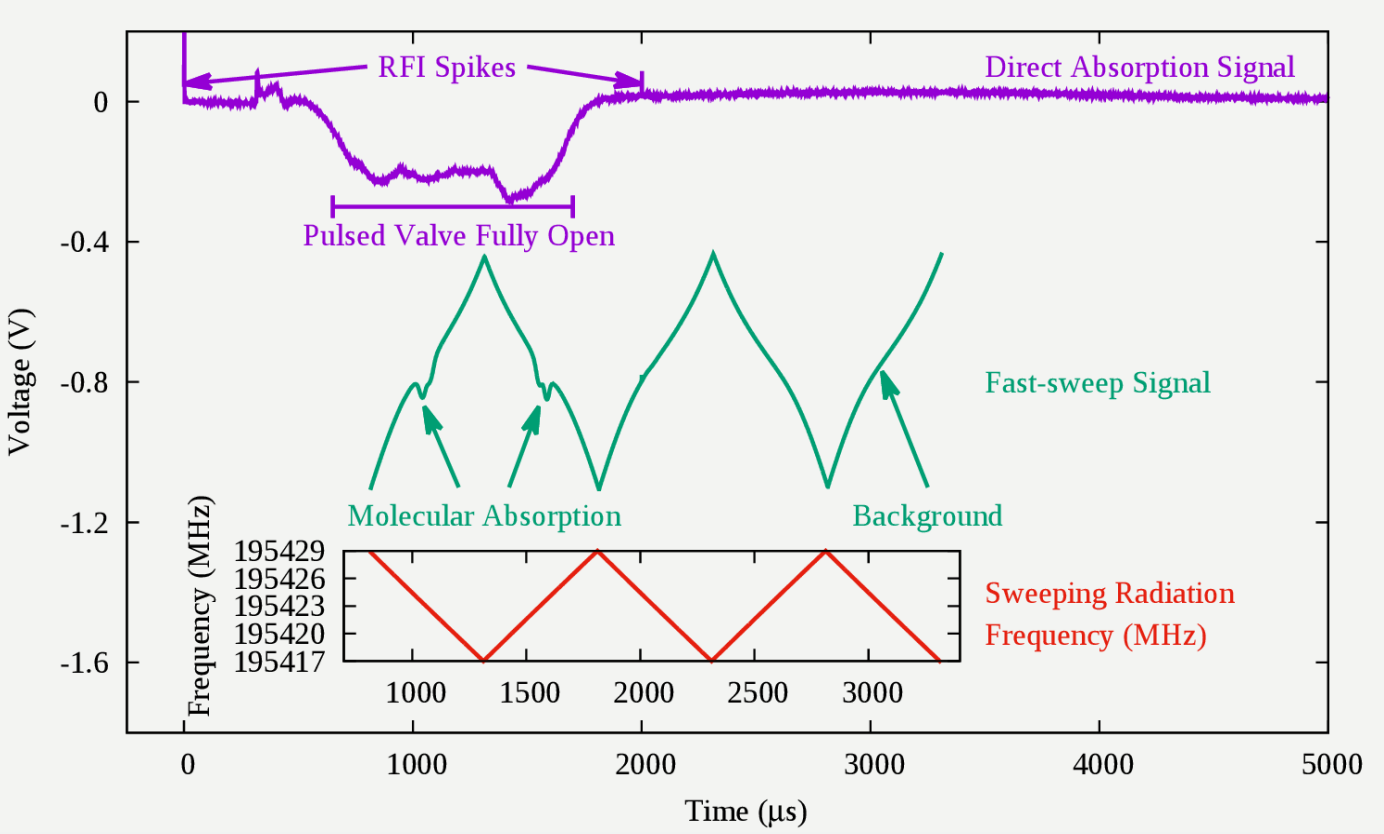


Fast Sweep Data Acquisition





Fast Sweep Data Acquisition



Advantage

Speed: ~100 times faster than Lock-in detection

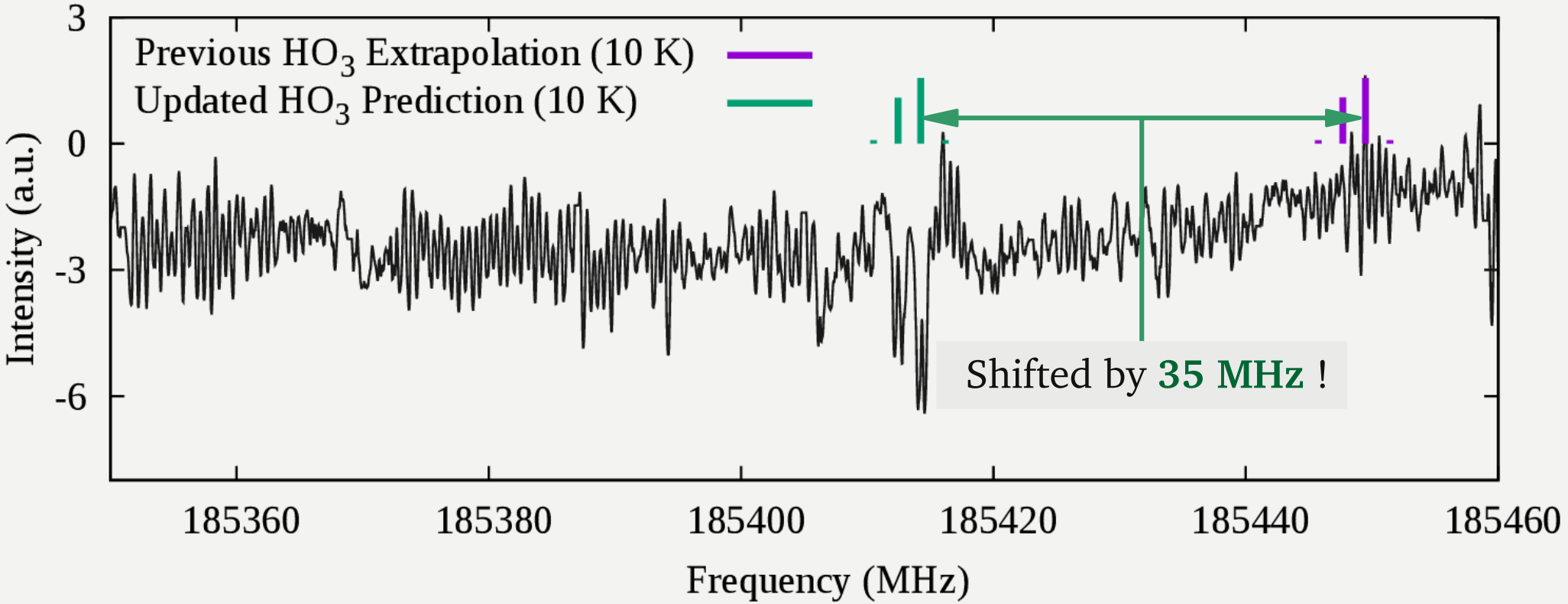
Disadvantage

Sensitivity: Unable to identify weak lines

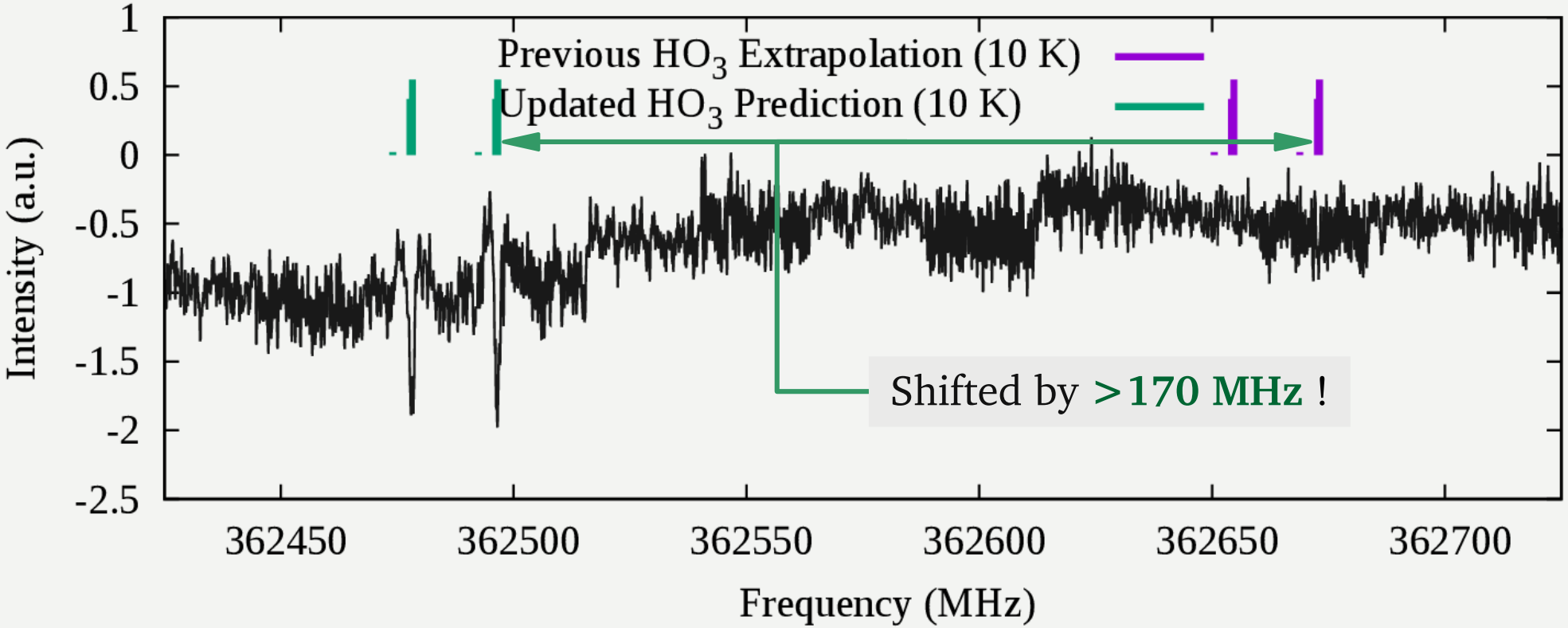
Baseline: Baseline is not completely clean and flat

Works for broadband line searching

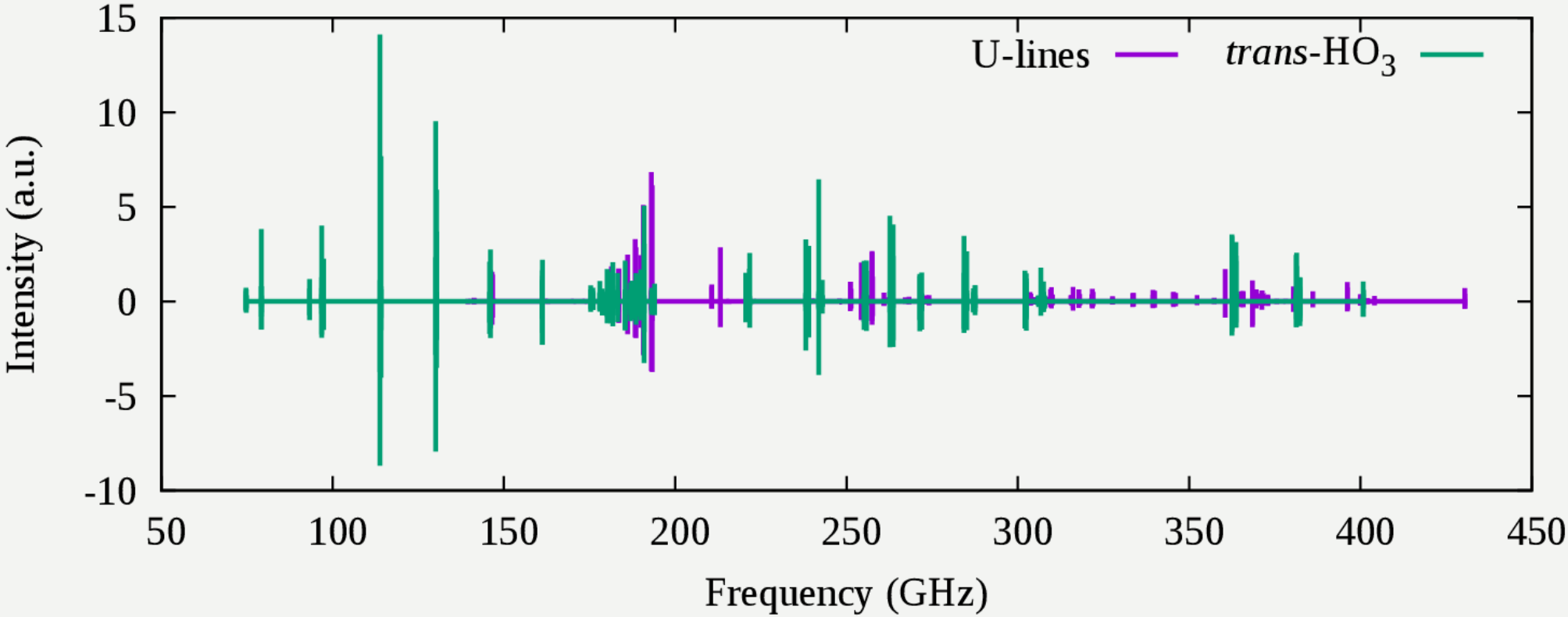
Search with Fast Sweep



Search with Fast Sweep



Follow-up Lock-in Detection – Full Spectrum



Updated Spectroscopic Constants

Constants (MHz)	This Study	Suma et al.	Difference	Constants (MHz)	This Study	Suma et al.	Difference
A	70781.17130(166)	70778.1652(23)	3.006	ε_{aa}	-1252.6930(42)	-1252.5858(58)	-0.107
B	9987.3738(59)	9986.9501(13)	0.424	ε_{bb}	-106.25162(197)	-106.2551(26)	-0.003
C	8749.7419(57)	8750.1580(7)	-0.416	ε_{cc}	-3.49782(186)	-3.4954(24)	0.002
Δ_N	0.0474845(222)	0.046461(30)	0.0010	$\lvert\varepsilon_{ab}+\varepsilon_{ba}\rvert/2$	42.554(81)	42.45(11)	0.10
Δ_{NK}	0.149515(122)	0.15335(40)	-0.0038	$\Delta^S_N\times10^3$	1.081(75)	1.00(10)	0.1
Δ_K	2.955986(257)	--		Δ^S_{NK}	-1.5719(305)	0.0544(15)	-1.62
$\delta_N\times10^3$	6.1547(114)	6.11(41)	0.1	Δ^S_{KN}	1.732(32)	--	
δ_K	0.20903(289)	--					
a_F	3.66069(240)	3.6587(30)	0.002	σ_{fit} (MHz)	0.0697	0.0054	
T_{aa}	10.1089(96)	8.4828(59)	1.626				
T_{bb}	-5.2215(93)	-6.8533(56)	1.632				

Summary

trans-HO_3 transitions (70 – 410GHz)

Fast Sweep Technique for Line Searching

Updated Spectroscopic Constants for *trans*-HO_3

U-lines Detected (Under Assignment)

Acknowledgement

NSF

Thank You for Your Attention

Q & A